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PATENT SPECIFICATION

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(19)

(54) IMPROVEMENTS RELATING TO ALKALI-RESISTANT GLASS COMPOSITIONS

(71) We, PILKINGTON BROTHERS LIMITED, a Company incorporated under the laws of Great Britain, of Prescot Road, St. Helens, Lancashire, England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to alkali-resistant glass compositions and particularly, though not exclusively, to such compositions which can be formed into glass fibres. It is known to include a proportion of zirconia (ZrO_2) in glass compositions for enhancing their resistance to alkalis. It is also known that the inclusion of substantial proportions of boron oxide (B_2O_3) and/or alkali metal oxides (M_2O) has a deleterious effect on the alkali resistance of the glass, although both these constituents have other favourable properties which have hitherto been considered to make their inclusion desirable. For example, both B_2O_3 and M_2O act as fluxes to aid melting and thus help to overcome the tendency of ZrO_2 to make melting difficult, and they can also improve the characteristics of the glass for drawing glass fibres.

It is an object of the present invention to provide glass compositions with a particularly high alkali resistance.

According to the present invention, a glass composition comprises, in weight percentages:—

SiO_2	45 to 65%
ZrO_2	6 to 20%
RO	20 to 45%

the total of $SiO_2 + ZrO_2 + RO$ being not less than 94% by weight of the glass, where RO represents at least one divalent oxide of the group consisting of CaO, MgO, SrO, BaO and ZnO, the amount of said divalent oxide or oxides lying within the ranges, in weight percentages: CaO 12 to 45%; MgO 0 to 14%; SrO 0 to 8%; BaO 0 to 10% and ZnO 0 to 5%; the balance (if any) of the composition consisting of other compatible constituents.

The balance of the composition may consist of at least one of the following constituents: TiO_2, Al_2O_3, B_2O_3, Fe_2O_3, F, and M_2O, where M_2O represents K_2O, Na_2O or Li_2O, the amount of any one of the said constituents not exceeding 5% by weight of the composition. Preferably the amount of M_2O does not exceed 3% by weight of the composition.

The glass compositions according to the invention thus contain relatively large proportions of ZrO_2, while being free from, or containing only low proportions of, B_2O_3 and M_2O. In spite of the absence or low level of these fluxing agents, it has proved possible to melt the glass compositions quite readily.

When subjected to standard tests for chemical durability in aqueous and in alkaline environments, such glass compositions have shown excellent results. It has also proved possible to form them into glass wool fibres, e.g. by high temperature blown type processes.

Specific embodiments of glass compositions in accordance with the invention will now be described by way of example.

The following Table 1 lists 18 glass compositions consisting of ZrO_2, SiO_2 and CaO, illustrating the use of four different values for ZrO_2 (18, 14, 10 and 8 weight %) with varying proportions of SiO_2 between 45 and 65 weight % and correspondingly inversely varying proportions of CaO between 45 and 21 weight %.

[Price 33p]

TABLE 2

Glass No. C 07		157 Mol	157 Wt. %	158 Mol	158 Wt. %	159 Mol	159 Wt. %	163 Mol	163 Wt.%
SiO_2		54	51.55	58	55.2	55	53.6	50	47.9
ZrO_2		7	13.7	7	13.7	5	10.0	7	13.7
CaO		39	34.75	35	31.1	40	36.4	43	38.4
MgO									
SrO									
BaO									
TiO_2									
Na_2O									
ZnO									
Al_2O_3									
Liquidus Temperature T_L °C		1405		1420		1450		1450	
Chemical Durability									
Reagent	Oxide extracted								
H_2O	Na_2O								
	SiO_2	1.0		1.0		0.6		1.2	
	CaO	0.63		0.65		1.1		0.73	
N/10 NaOH	SiO_2	0.6		0.8		1.6		0.05	
	CaO	0.26		0.26		0.24		0.31	
N NaOH	SiO_2	1.4		1.25		1.2		1.25	
	CaO	0.59		0.74		0.81		0.75	

TABLE 2 (continued)

Glass No. C 07	179 Mol	179 Wt. %	183 Mol	183 Wt. %	186 Mol	186 Wt. %	199 Mol	199 Wt.%
SiO_2	56	53.7	58	55.0		58.2	54	51.4
ZrO_2		13.75	7	13.63		14.0	7	13.66
CaO	30	26.8	28	24.8		22.8	32	28.44
MgO	5	3.2	5	3.2			5	3.19
SrO			2	3.3			2	3.28
BaO								
TiO_2	2	2.55						
Na_2O						5.0		
ZnO								
Al_2O_3								
Liquiuus Temperature T_L °C	1395		1418		1370		1400	
Chemical Durability								
Reagent / Oxide extracted								
H_2O Na_2O					0.33			
H_2O SiO_2			0.25		0.8		1.0	
H_2O CaO	1.02		0.35		0.42		0.37	
N/10 NaOH SiO_2	1.15		0.85		1.2		0.8	
N/10 NaOH CaO	0.25		0.1		0.21		0.2	
N NaOH SiO_2	1.3				2.0		0.4	
N NaOH CaO	0.95		0.25		0.5		0.25	

TABLE 2 (continued)

Glass No. C-07		206 Mol	206 Wt. %	208 Mol	208 Wt. %	209 Mol	209 Wt. %	211 Mol	211 Wt. %
SiO_2		58	58.48		65.0		65.0		52.0
ZrO_2		7	13.23		10.0		12.0		18.0
CaO		28	25.0		20.0		20.0		29.0
MgO		5	3.21						
SrO									
BaO									
TiO_2									
Na_2O					5.0		3.0		1.0
ZnO		2	2.59						
Al_2O_3									
Liquidus Temperature T_L °C		1410							
Chemical Durability:									
Reagent	Oxide extracted								
H_2O	Na_2O				0.22		0.135		
	SiO_2		0.4		0.7		0.25		
	CaO		0.2		0.19		0.125		
	BaO								
	ZnO		0.5						
N/10 NaOH	SiO_2		0.5		1.15		1.05		
	CaO		0.15		0.1		0.1		
	MgO								
	BaO								
	ZnO		0.1						
N NaOH	SiO_2		2.85		2.25		2.25		
	CaO		0.3		0.38		0.25		
	MgO								
	BaO								
	ZnO		0.15						

The liquidus temperatures of glasses C/07/209 to 216 inclusive were not precisely measured, but it was ascertained that they all fell within the range from 1400°C to 1500°C. The chemical durability of glasses C/07/211 and 213 was not measured because these glasses are very similar to glass 212, differing only in the content of ZrO_2 with consequential adjustment to the SiO_2 content, and they can consequently be confidently predicted to have similar chemical durability, 211 being slightly less good due to its lower ZrO_2 and 213 being slightly better due to its higher ZrO_2 content.

When using the maximum permissible amount of SiO_2 (65 weight %) a proportion of up to 5 weight % Na_2O may be included, as in glasses C/07/208 and 209, to improve the drawing characteristics of the glass and thereby facilitate the formation of fibres. These glasses also contain the minimum permissible amount of RO (20 weight %). In general, the amount of RO increases as the amount of SiO_2 is reduced. As shown by the foregoing Examples, CaO may vary between 19 and 45% and up to 14% of the RO may consist of MgO, as in glass C/07/176. Up to 10% of the RO can be BaO, up to 8% of the RO can be SrO, and up to 5% of the RO can be ZnO, if desired. With MgO or SrO present, a slight lowering of the liquidus temperature can be achieved, which is beneficial for formation of glass fibres. A small amount of TiO_2 can also be included, as in glass C/07/179, to produce a similar lowering of the liquidus temperature, but TiO_2 also tends to reduce the alkali resistance so it can only be used to a limited extent, i.e. up to 5 weight %. Al_2O_3 produces similar effects, as seen from glass C/07/176.

B_2O_3 or F_2 could also be included in amounts of up to 5 weight % to assist melting. Fe_2O_3 may be present in the customary small amounts (up to 0.5 weight %) which result from the normal impurities in raw materials.

WHAT WE CLAIM IS:—

1. A glass composition which comprises, in weight percentages:—

SiO_2	45 to 65%
ZrO_2	6 to 20%
RO	20 to 45%

the total of $SiO_2 + ZrO_2 + RO$ being not less than 94% by weight of the glass, where RO represents at least one divalent oxide of the group consisting of CaO, MgO, SrO, BaO and ZnO, the amount of said divalent oxide or oxides lying within the ranges, in weight percentages: CaO 19 to 45%; MgO 0 to 14%; SrO 0 to 8%; BaO 0 to 10%, and ZnO 0 to 5%, the balance (if any) of the composition consisting of other compatible constituents.

2. A glass composition according to Claim 1, wherein the balance of the composition consists of at least one of the following constituents: TiO_2, Al_2O_3, B_2O_3, Fe_2O_3, F_2 and M_2O, where M_2O represents K_2O, Na_2O or Li_2O, the amount of any one of the said constituents not exceeding 5% by weight of the composition.

3. A glass composition according to Claim 2, wherein the amount of M_2O does not exceed 3% by weight of the composition.

4. A glass composition according to Claim 2, wherein $SiO_2 = 65\%$ and $CaO = 20\%$ and the composition also contains 5% Na_2O by weight.

5. An alkali-resistant glass composition in accordance with any one of the compositions listed in Table 1 or Table 2.

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